An Explicit Hydrogen-Bonding Non-random Lattice-Fluid Equation of State and Its Applications[1]

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ABSTRACT

The representation of hydrogen-bonding contribution generally involves the number of hydrogen-bonding pair that requires implicit computation when more than one type of bonds is present. To reduce the computational burden associated with the solution of a set of nonlinear implicit equations, a free energy expansion method is proposed for Veytsman statistics in the present study. Based on the normalized Veytsman statistics of the present authors, the Helmholtz free energy for association was expanded around a reference value. The lattice-compatible expanded Veytsman term was then combined with the explicit non-random lattice-fluid model of present authors to obtain equations for pressure and chemical potential. Calculated vapor-liquid equilibria using the expansion were found to closely agree with rigorous calculation results and with experimental values for alkane-alkanol mixtures.

KEY WORDS : alkane-alkanol, association, equation of state, hydrogen-bonding, lattice fluid model, vapor-liquid equilibria

1. INTRODUCTION

Phase equilibria and thermophysical properties involving molecules with specific interactions are of importance in many industrial systems. However, the equation of state approach to such systems has long been limited to vapor phase [1]. Recent interests in equations of state approach have been focused on studies applicable to both vapor and liquid phase. Among the most successful methods are the statistical associating fluid theory (SAFT) [2] and hydrogen-bonding non-random lattice fluid theory (NLF-HB) [3]. In Helmholtz free energy expressions, both theories have association terms that are implicit for mixtures with more than one type of hydrogen bonds.

The non-association part of NLF-HB was derived from the Guggenheim combinatory [4] and made explicit by expanding Helmholtz free energy around the reference athermal solution [5,6]. The hydrogen-bonding contribution was derived from Veytsman statistics [7] that are compatible with lattice statistics. Recently Lee et al. [8] pointed out that Veytsman contribution still has non-zero contribution even if the hydrogen-bonding free energy tends to zero and proposed a normalization scheme. Furthermore they proposed a method for the explicit evaluation of hydrogen-bonding pairs in the Veytsman terms. This evaluation method could be very helpful in removing the numerical difficulties associated with the solution of implicit equations for Veytsman terms. Yet, a more consistent method would be based on an expansion method of Helmholtz free energy. In this study, we develop the free energy expansion scheme for the problem with one type of hydrogen bonds and explore the consequences for mixtures with aliphatic alcohols.

2. Derivation

We consider a c component mixture in the lattice of fixed cell volume V_H and the coordination number z. Component i in a c-component mixture has r_i segments. The surface area parameter q_i of component i is related by the relation $2(r_i\text{-}1)=z(r_i\text{-}q_i)$. The interaction energy between segments of components i and j is ε_{ij}. A segment may be a hydrogen donor or acceptor. The number of hydrogen donor groups of type k in species i is d_k^i and the number of acceptor groups of type l in species j is a_l^j. The total number of donor types is m and that of acceptor types is n. The hydrogen-bonding free energy is A_{ij}^{HB}.

The lattice configurational partition function is assumed as the product of physical and hydrogen-bonding contributions.

$$\Omega^c = \Omega_P^c \Omega_{HB}^c \tag{1}$$

The physical contribution was derived from Guggenheim combinatory and made explicit by expansion around the reference athermal solution and by retaining terms up to the second order [5,6].

The implicit formulation of the chemical contribution from Veytsman statistics [7] was proposed by Lee et al. [3]. The total number of donor groups of type k (N_d^k) and that of acceptor groups of types l (N_a^l) are given by

$$N_d^k = \sum_i^c d_k^i N_i \,, \quad N_a^l = \sum_j^c a_l^j N_j \tag{2}$$

We also define the total number of donor-acceptor pair (N_{HB}), unpaired donors (N_{i0}^{HB}) and unpaired acceptors (N_{0j}^{HB}) as functions of the number of i-j hydrogen bond pair (N_{ij}^{HB}).

$$N_{HB} = \sum_i^m \sum_j^n N_{ij}^{HB} \ , \quad N_{i0}^{HB} = N_d^i - \sum_j^n N_{ij}^{HB} \ , \quad N_{0j}^{HB} = N_a^j - \sum_i^m N_{ij}^{HB} \qquad (3)$$

According to the normalized Veytsman statistics proposed later by Lee et al. [8], the hydrogen-bonding contribution is written as,

$$\Omega_{HB}^c = \frac{N_r^{N_{HB0}}}{N_r^{N_{HB}}} \prod_i^m \frac{N_{i0}^{HB0}!}{N_{i0}^{HB}!} \prod_j^n \frac{N_{0j}^{HB0}!}{N_{0j}^{HB}!} \prod_i^m \prod_j^n \frac{N_{ij}^{HB0}!}{N_{ij}^{HB}!} \exp(-\beta N_{ij}^{HB} A_{ij}^{HB}) \qquad (4)$$

where,

$$N_r = N_0 + \sum_{i=1}^c r_i N_i \qquad (5)$$

The maximization condition leads to

$$N_{ij}^{HB} N_r = N_{i0}^{HB} N_{0j}^{HB} \exp(-\beta A_{ij}^{HB})$$

$$= (N_d^i - \sum_{k=1}^n N_{ik}^{HB})(N_a^j - \sum_{k=1}^m N_{kj}^{HB}) \exp(-\beta A_{ij}^{HB}) \quad (i=1,2,..,m,\ j=1,2,..,n) \qquad (6)$$

The hydrogen-bonding contribution to Helmholtz free energy is

$$\beta A_{HB}^c = -\ln \Omega_{HB}^c$$

$$= (N_{HB} - N_{HB0})(\ln N_r + 1) + \sum_i^m (N_{i0}^{HB} \ln N_{i0}^{HB} - N_{i0}^{HB0} \ln N_{i0}^{HB0}) + \sum_i^n (N_{0i}^{HB} \ln N_{0i}^{HB} - N_{0i}^{HB0} \ln N_{0i}^{HB0})$$

$$+ \sum_i^m \sum_j^n (\beta A_{ij}^{HB} N_{ij}^{HB} + N_{ij}^{HB} \ln N_{ij}^{HB} - N_{ij}^{HB\,0} \ln N_{ij}^{HB\,0}) \qquad (7)$$

where quantities with superscript or subscript *HB0* come from the solution of Eq 5 with $A_{ij}^{HB} = 0$.

For the explicit formulation of the chemical or hydrogen-bonding contribution, we expand Helmholtz free energy around a reference free energy.

$$\beta A_{HB}^C = \beta A_{HBR}^C + \sum_i^m \sum_j^n \left(\frac{\partial \beta A_{HB}^C}{\partial A_{ij}^{HB}} \right)_{HBR} (A_{ij}^{HB} - A^{HBR}) + \sum_k^m \sum_l^n \sum_i^m \sum_j^n \left[\frac{\partial}{\partial A_{kl}^{HB}} \left(\frac{\partial \beta A_{HB}^C}{\partial A_{ij}^{HB}} \right) \right]_{HBR} (A_{ij}^{HB} - A^{HBR})(A_{kl}^{HB} - A^{HBR}) \quad (8)$$

The subscript HB indicates the hydrogen-bonding contribution for the system and the superscript HB the contibution for donor-acceptor pairs. Subscript and superscript HBR means the value at the reference state. The reference Helmholtz free energy is obtained from Eq 6 by replacing quantities with superscript or subscript HB by HBR that are obtained from the solution of Eq 5 by setting A_{ij}^{HB} to a constant reference value A^{HBR} independent of donor or acceptor type. As shown in the appendix N_{ij}^{HB0} or N_{ij}^{HBR} is readily obtained explicitly.

The pressure of system and the chemical potential of component i also can be parted into the additive physical and chemical contributions,

$$P = P_P + P_{HB} \qquad (9)$$

$$\mu_i = \mu_i^P + \mu_i^{HB} \qquad (10)$$

where the subscript and superscript P denotes the physical contribution. The physical contribution of Helmholtz free energy is presented from the NLF model of You et al. [5,6]. For the simplest system with one donor type and one acceptor type the pressure for chemical part can be derived by the standard method.

$$P_{HB} = -\left(\frac{\partial A_{HB}^c}{\partial V} \right)_T = -\frac{1}{V_H} \left(\frac{\partial A_{HB}^c}{\partial N_0} \right)_T$$

$$= -\frac{\nu_{HBR}\rho}{V_H\beta} + \frac{\exp(\beta A^{HBR})}{V_H}\left[\frac{N_{11}^{HBR}}{N_r\exp(\beta A^{HBR}) + N_{10}^{HBR} + N_{01}^{HBR}}\left(A_{11}^{HB} - A^{HBR}\right)\right.$$

$$\left. + \frac{N_{11}^{'} N_r \exp(\beta A^{HBR}) + 2N_{11}^{HBR} N_{11}^{'} + (N_{10}^{HBR} + N_{01}^{HBR})(N_{11}^{'} + N_{11}^{HBR}\beta)}{(N_r\exp(\beta A^{HBR}) + N_{10}^{HBR} + N_{01}^{HBR})^2}(A_{11}^{HB} - A^{HBR})^2\right] \quad (11)$$

where,

$$\rho = \sum_{i=1}^{c}\rho_i\,, \quad \rho_i = N_i r_i / N_r \quad (12)$$

$$\nu_{HBR} = (N_{HBR} - N_{HB0}) / \sum_{i=1}^{c} N_i r_i \quad (13)$$

$$N_{11}^{'} = -N_{11}^{HBR} N_r \beta \exp(\beta A^{HBR}) \Big/ \left(N_r\exp(\beta A^{HBR}) + N_{10}^{HBR} + N_{01}^{HBR}\right) \quad (14)$$

The chemical part in Eq (10) is derived by well-known relation and expressed as

$$\beta\mu_i^{HB} = \left(\frac{\partial\beta A_{HB}^{C}}{\partial N_i}\right)_{T,V,N_j} = \left(\frac{\partial\beta A_{HB}^{C}}{\partial N_i}\right)_{T,N_j} - \left(\frac{\partial\beta A_{HB}^{C}}{\partial V}\right)_{T,N}\left(\frac{\partial V}{\partial N_i}\right)_{T,N_j}$$

$$= -d_1^i \ln\frac{N_{10}^{HB0}}{N_{10}^{HBR}} - a_1^i \ln\frac{N_{01}^{HB0}}{N_{01}^{HBR}} + \frac{d_1^i N_{01}^{HBR} + a_1^i N_{10}^{HBR}}{N_r\exp(\beta A^{HBR}) + N_{10}^{HBR} + N_{01}^{HBR}}\beta\left(A_{11}^{HB} - A^{HBR}\right)$$

$$- \frac{\left(d_1^i + a_1^i\right)\left(N_r\exp(\beta A^{HBR}) + N_{10}^{HBR} + N_{01}^{HBR}\right)N_{11}^{'} + \left(N_r\beta\exp(\beta A^{HBR}) - 2N_{11}^{'}\right)\left(d_1^i N_{01}^{HBR} + a_1^i N_{10}^{HBR}\right)}{\left(N_r\exp(\beta A^{HBR}) + N_{10}^{HBR} + N_{01}^{HBR}\right)^2}$$

$$\times\beta\left(A_{11}^{HB} - A^{HBR}\right)^2 \quad (15)$$

Eqs.(11) and (15) appear complicated, but are advantages over rigorous NLF-HB EOS in computation. The derivatives in Eq (8) are evaluated at the reference state and the number of hydrogen bond balance equations at reference state, Eq (6), are readily solved explicitly regardless of the number of donor type and acceptor type.

3. Results and Discussions

We set the coordination number z at 10 and the unit lattice volume V_H at 9.75cm^3/mol. The hydrogen bonding Helmholtz free energies are defined by following equation.

$$A^{HBR} = U^{HBR} - TS^{HBR} \quad (16)$$

$$A_{ij}^{HB} = U_{ij}^{HB} - TS_{ij}^{HB} \quad (17)$$

The reference values are set to U^{HBR} = –20.3 *kJ/mol* and S^{HBR} = –21.55 *J/mol·K*. U_{ij}^{HB} = -25.1 *kJ/mol* from Renon and Prausnitz [9] and S_{ij}^{HB} = -26.5 *J/mol·K* from Panayiotou [10] for 1-alkanols. Two molecular parameter, r_i and ε_{ii}, are fitted to saturated liquid density and vapor pressure data for subcritical region and pressure-volume isotherm data for supercritical region. The temperature dependency is correlated by the following form [11],

$$r_1 = r_a + r_b(T - T_0) + r_c\left[T\ln(T_0/T) + T - T_0\right] \quad (18)$$

$$\varepsilon_{11} = e_a + e_b(T - T_0) + e_c\left[T\ln(T_0/T) + T - T_0\right] \quad (19)$$

where the reference temperature, T_0, is 298.15 K. Temperature coefficients in Eqs.(18) and (19) for 1-alkanols and alkanes are listed in Table 1. For mixtures, an interaction parameter between different two molecules is defined by

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{0.5}(1-\lambda_{12}) \quad (20)$$

and is fitted to binary VLE data.

Fig. 1 shows comparisons by four different calculations. One is the result of NLF calculations in which hydrogen-bonding consideration is not included. The result is seen inferior to the other calculations with hydrogen-bonding corrections. The second one is the result of rigorous evaluation of hydrogen-bonding effects as proposed by Yeom et al. [3] and by Lee et al. [8]. These two methods give essentially identical results. In the third method, the number of hydrogen bonds is explicitly evaluated. The last one is by the present expansion of Helmholtz free energy. The present method is seen to give essentially the same results as the rigorous methods. It is also a more consistent method in that both physical and chemical terms are expanded in Helmholtz free energy and terms up to the second order are retained. When compared with data, pentanol-pentane system in Fig. 1 gives good results.

Results of isothermal P-y calculations by the present free energy expansion method for alcohol-alkane mixture are summarized in Table 2. N-Hexane and methanol system shows somewhat large deviations. Ethanol and n-hexane mixture shows a large pressure deviation, but the system pressure is very low. Other than these systems, the results are seen generally acceptable.

4. Conclusion

In the non-random lattice fluid hydrogen-bonding model, Veytsmann statistics defines a set of nonlinear equations to solve for the number of hydrogen bonds when more than one type of donor-acceptor pairs are present. To circumvent the difficulties associated with the solution, a free energy expansion method was proposed for explicit solutions in this study.. When applied to vapor-liquid equilibria, the expansion method was found to give good approximation to the rigorous solution and to describe the phase equilibrium behavior accurately in most cases for alkane-alkanol mixtures.

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List of symbols

A	Helmholtz free energy
a, d	number of acceptor groups and donor groups in a molecule, respectively
N_a, N_d	number of acceptor groups and donor groups in system, respectively
N_r	number of site in lattice
N_0	number of hole in lattice
r	segment number
V_H	unit lattice volume
z	coordination number
Greeks letters	
ε	interaction energy parameter
λ	binary interaction parameter
μ	chemical potential
ν_{HB}	defined by eq.(13)

Ω	partition function
Superscripts	
C	configurational property
HB	chemical contribution by HB
HB0	zero HB Helmholtz free energy state value
HBR	reference HB Helmholtz free energy state value
i,j,k,l	index for component, donor group or acceptor group
Subscripts	
HB	chemical contribution by HB
HB0	zero HB Helmholtz free energy state value
HBR	reference HB Helmholtz free energy state value
i,j,k,l	index for component, donor group or acceptor group
ij, kl	interaction pair

References

[1] J.G. Hayden and J.P. O'Connell, Ind. Eng. Chem. Process Des. Dev., 14 (1975) 221.
[2] W.G. Chapman, K.E. Gubbins, G. Jackson, and M. Radosz, Ind. Eng. Chem, Res., 29 (1990) 1709.
[3] M.S. Yeom, K.-P. Yoo, B.H. Park, and C.S. Lee, Fluid Phase Equilib. 158 (1999) 143.
[4] E.S. Guggenheim, Mixtures, Clarendon Press, Oxford, 1952.
[5] S.S. You, K.-P. Yoo, and C.S. Lee, Fluid Phase Equilib. 93 (1994) 193.
[6] S.S. You, K.-P. Yoo, and C.S. Lee, Fluid Phase Equilib. 93 (1994) 215.
[7] B.A. Veytsman, J. Phys. Chem. 94 (1990) 8499.
[8] C.S. Lee, K.-P. Yoo, B.H. Park, and J.W. Kang, J. Phys. Chem. Submitted.
[9] H. Renon, and J.M. Prausnitz, Chem. Eng. Sci. 22 (1967) 299.
[10] C. Panayiotou, J. Phys. Chem. 92 (1988) 2960.
[11] H.V. Kehiaian, J.P.E. Grolier, and G.C. Bebson, J. Chem, Phys. 75 (1978) 1031.
[12] A.-D. Leu, D.B. Robinson, S.Y.-K. Chung, and C.-J. Chen, Can. J. Chem. Eng., 70 (1992) 330.
[13] N. Ishii, J. Soc. Chem. Ind. Jan. 38 (1935) 659.
[14] M. Ronc and G.R. Ratcliff, Can. J. Chem. Eng., 54 (1976) 326.
[15] N.A. Smirnova and L.M. Kurtynina, Zh. Fiz. Khim., 43 (1969) 1883.
[16] A. Kumar and S.S. Katti, Indian J.Chem., 19A (1980) 795.
[17] S.G. Sage and G.A. Ratcliff, J. Chem. Eng. Data 21 (1976) 71.
[18] M. Scheller, H. Schuberth, and H.G. Koennecke, J. Prakt. Chem., 311 (1969) 974.
[19] A.M. Kinyukhin, T.M. Lesteva, N.P. Markuzin, and L.S. Budantseva, Prom-st. Sint. Kauch. 7 (1982) 4.
[20] S. Ernatova, J. Linek, and I. Wichterle, Fluid Phase Equilib., 74 (1992) 127.

Appendix

N_{HBR} is obtained by solving quadratic equation after summing Eq (6) in i and j .

$$N_{HBR} = \frac{1}{2}\left[N_r \exp(\beta A^{HBR}) + N_a + N_d - \left\{ \left(N_r \exp(\beta A^{HBR}) + N_a + N_d \right)^2 - 4 N_a N_d \right\}^{1/2} \right] \quad \text{(A1)}$$

By summing both sides of Eq (6) once in i and once in j we get expressions for $\sum_{i=1}^{m} N_{ij}^{HBR}$ and $\sum_{j=1}^{n} N_{ij}^{HBR}$.

$$N_r \exp(\beta A^{HBR}) \sum_{i=1}^{m} N_{ij}^{HBR} = (N_d - N_{HBR})(N_a^j - \sum_{k=1}^{m} N_{kj}^{HBR}) \quad \text{(A2)}$$

$$N_r \exp(\beta A^{HBR}) \sum_{j=1}^{n} N_{ij}^{HBR} = (N_d^i - \sum_{k=1}^{n} N_{ik}^{HBR})(N_a - N_{HBR}) \quad \text{(A3)}$$

Eqs. (A2) and (A3) are simultaneously rearranged in terms of N_{HBR} and readily substituted into Eq (6) then we obtain the following equation.

$$N_{ij}^{HBR} = \frac{N_d^i N_a^j}{N_r \exp(\beta A^{HBR})} \left(1 - \frac{N_a - N_{HBR}}{N_r \exp(\beta A^{HBR}) + N_a - N_{HBR}} \right) \left(1 - \frac{N_d - N_{HBR}}{N_r \exp(\beta A^{HBR}) + N_d - N_{HBR}} \right) \quad \text{(A4)}$$

These expressions give N_{ij}^{HB0} by setting A^{HBR} =0 and $N_{HBR} = N_{HB0}$.

Table 1. Temperature coefficients of molecular parameters

Chemicals	e_a	e_b	e_c	r_a	r_b	r_c	Range(K)
Propane	84.774	0.0161	-0.1399	6.827	-0.0005	0.0077	115-345
n-Pentane	94.484	0.0369	0.0189	9.924	-0.0021	0.0012	303-443
n-Hexane	97.278	0.0313	-0.0245	11.460	-0.0015	0.0061	273-473
n-Heptane	99.068	0.0352	-0.0187	13.035	-0.0019	0.0060	273-513
n-Decane	101.689	0.0529	0.0125	17.805	-0.0034	0.0057	368-598
Methanol	113.282	0.0156	-0.1085	3.754	0.0009	0.0006	215-465
Ethanol	106.213	0.0146	-0.0544	5.357	0.0002	0.0034	239-489
1-butanol	107.495	0.0006	-0.0914	8.469	0.0014	0.0054	275-505
1-pentanol	107.165	0.0337	-0.0256	10.020	-0.0001	0.0048	295-565
1-octanol	108.068	0.0325	-0.0346	15.061	0.0012	0.0099	313-573

Table 2. Comparison of results with experimental data

System	T(K)	λ_{12}	AADP[a]	AADY[b]	References
Methanol + propane	310.70	0.060	2.11	0.0259	[12]
Ethanol + *n*-hexane	293.15	0.033	6.18	0.0116	[13]
1-butanol + *n*-pentane	303.15	0.019	0.10	0.0017	[14]
1-butanol + *n*-hexane	298.15	0.024	0.10	0.0295	[15]
1-butanol + *n*-heptane	348.15	0.033	2.89	0.0398	[16]
1-pentanol + *n*-pentane	303.15	0.017	0.10	0.0144	[14]
1-pentanol + *n*-hexane	323.15	0.017	0.07	0.0057	[17]
n-Hexane + methanol	333.15	0.071	5.27	0.0676	[18]
1-octanol + *n*-heptane	313.15	0.008	1.27	0.0570	[19]
n-Decane + 1-butanol	358.15	0.022	0.09	0.0127	[20]

[a] $AADP = (100/N)\sum_i^N |P_i^{cal} - P_i^{\exp}| / P_i^{\exp}$ [b] $AADY = (1/N)\sum_i^N |Y_i^{cal} - Y_i^{\exp}| / Y_i^{\exp}$

Figure captions

Figure 1. Comparison of experimental data with calculated NLF and NLF-HB EOSs for 1-pentanol + *n*-pentane system at 303.15 K

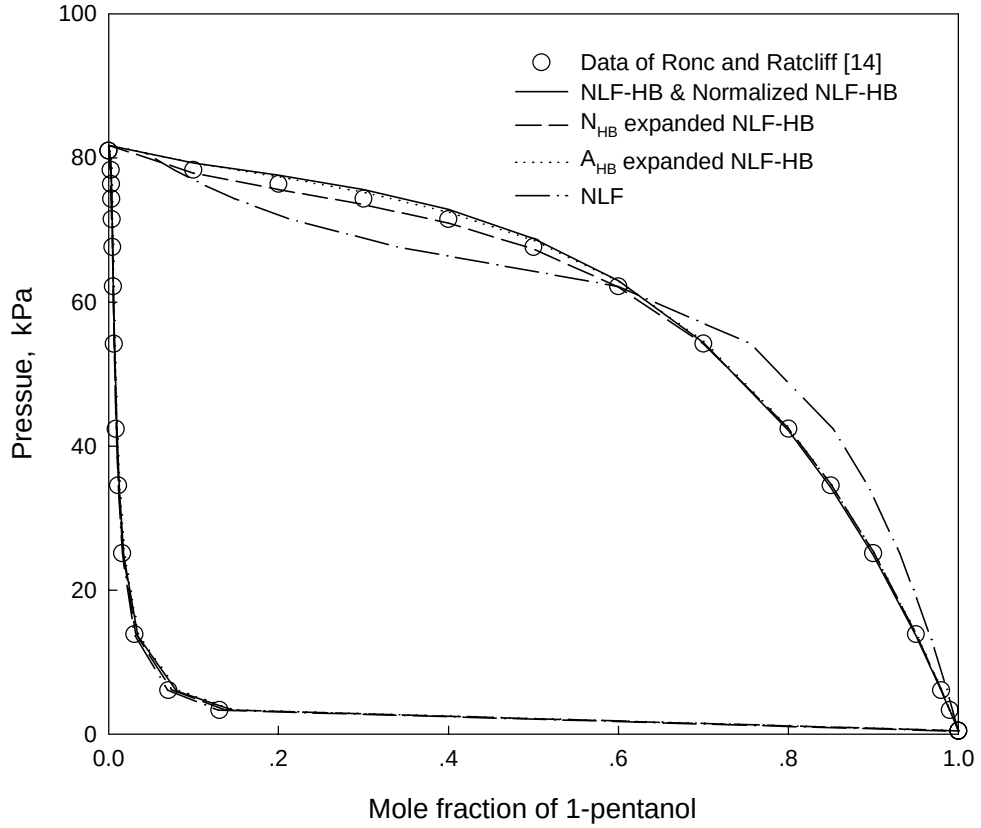

Figure 1. Comparison of experimental data with calculated NLF and NLF-HB EOSs for 1-pentanol + n-pentane system at 303.15 K